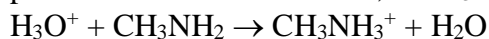


## ANSWERS: Titrations curves

1) a) At point A,  $[\text{CH}_3\text{NH}_2] \approx [\text{CH}_3\text{NH}_3^+]$ . So the solution has buffering properties in the proximity of point A. When HBr is added, the  $\text{H}_3\text{O}^+$  is consumed:



Since the  $\text{H}_3\text{O}^+$  is removed from the solution (neutralised), the pH does not change significantly.

b)  $[\text{H}_3\text{O}^+] = 10^{-11.8} = 1.58 \times 10^{-12}$

$$K_a = \frac{[\text{CH}_3\text{NH}_2][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{NH}_3^+]} \\ = \frac{[\text{CH}_3\text{NH}_2][\text{H}_3\text{O}^+]}{[\text{OH}^-]}$$

$$2.29 \times 10^{-11} = \frac{[\text{CH}_3\text{NH}_2] \cdot (10^{-11.8})^2}{1 \cdot 10^{-14}} \\ [\text{CH}_3\text{NH}_2] = \frac{(2.29 \cdot 10^{-11}) \cdot (1 \cdot 10^{-14})}{(10^{-11.8})^2} \\ = 0.0912 \text{ mol L}^{-1}$$

OR

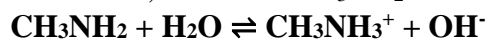
$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{10^{-14}}{10^{-11.8}} \\ = 6.31 \times 10^{-3} \text{ mol L}^{-1}$$

$$K_b = \frac{[\text{OH}^-]^2}{[\text{CH}_3\text{NH}_2]} \\ 4.37 \times 10^{-4} = \frac{(6.31 \cdot 10^{-3})^2}{[\text{CH}_3\text{NH}_2]} \\ [\text{CH}_3\text{NH}_2] = \frac{(6.31 \cdot 10^{-3})^2}{4.37 \cdot 10^{-4}} \\ [\text{CH}_3\text{NH}_2] = 0.0912 \text{ mol L}^{-1}$$

c)  $\text{CH}_3\text{NH}_3^+$ ,  $\text{Br}^-$ ,  $\text{CH}_3\text{NH}_2$ ,  $\text{H}_3\text{O}^+$

**At the start**, before addition of HBr there is a solution of weak base ( $\text{CH}_3\text{NH}_2$ ) which only partially reacts with water to produce a relatively low concentration of ions.

As a result, the initial  $\text{CH}_3\text{NH}_2$  solution will be a poor electrical conductor.



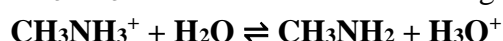
Therefore species present are  $\text{CH}_3\text{NH}_2 > \text{OH}^- \geq \text{CH}_3\text{NH}_3^+ > \text{H}_3\text{O}^+$

**At point B**, there is a solution of the salt  $\text{CH}_3\text{NH}_3\text{Br}$  present which is dissociated completely into ions.

Therefore there is a relatively high concentration of ions ( $\text{CH}_3\text{NH}_3^+$  and  $\text{Br}^-$ ) present in the solution, so it will be a good electrical conductor / electrolyte.



$\text{CH}_3\text{NH}_3^+$  reacts with water according to the equation



Species present are  $\text{Br}^- > \text{CH}_3\text{NH}_3^+ > \text{H}_3\text{O}^+ \geq \text{CH}_3\text{NH}_2 > (\text{OH}^-)$

2) a)

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \quad \bullet \quad \text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

$$[\text{H}_3\text{O}^+] = \sqrt{1.74 \cdot 10^{-5} \cdot 0.0896} \text{ mol L}^{-1} \\ = 1.25 \cdot 10^{-3} \text{ mol L}^{-1}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = 2.90$$

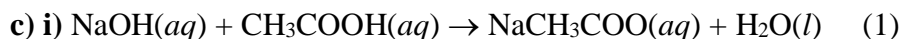
**b)** Halfway to equivalence point, half of the ethanoic acid has been used up. There are now equimolar quantities of ethanoic acid and sodium ethanoate.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

According to the equation when  $[\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COO}^-]$

then  $K_a = [\text{H}_3\text{O}^+]$

So  $\text{p}K_a = \text{pH}$ .



$[\text{CH}_3\text{COO}^-]$  increases as it is formed in reaction (1).

$[\text{Na}^+]$  increases as NaOH is added (1).

$[\text{CH}_3\text{COOH}]$  decreases as it reacts with NaOH (1).

$[\text{H}_3\text{O}^+]$  decreases because  $[\text{CH}_3\text{COO}^-] / [\text{CH}_3\text{COOH}]$  increases and  $K_a$  is a constant.

$[\text{OH}^-]$  increases because  $[\text{H}_3\text{O}^+]$  decreases and  $[\text{H}_3\text{O}^+][\text{OH}^-]$  is constant.

**c) ii)**  $n(\text{CH}_3\text{COOH at start}) = 0.0896 \times 20 \times 10^{-3}$   
 $= 1.79 \times 10^{-3} \text{ mol}$

$n(\text{NaOH added}) = 0.1 \times 5 \times 10^{-3}$   
 $= 5 \times 10^{-4} \text{ mol}$

After 5 mL NaOH added:

$n(\text{CH}_3\text{COOH}) = 1.29 \times 10^{-3} \text{ mol}$

$n(\text{CH}_3\text{COO}^-) = 5 \times 10^{-4} \text{ mol}$

$[\text{CH}_3\text{COOH}] = 0.0516 \text{ mol L}^{-1}$

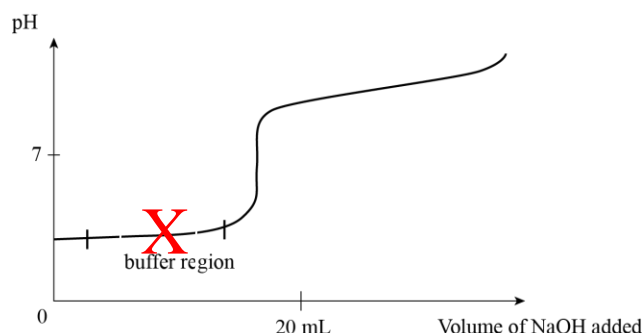
$[\text{CH}_3\text{COO}^-] = 0.0200 \text{ mol L}^{-1}$

$[\text{H}_3\text{O}^+] = 4.48 \times 10^{-5} \text{ mol L}^{-1}$

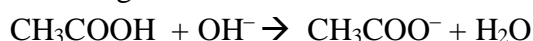
$\text{pH} = 4.35$

Candidates will not be penalised for not calculating concentrations.

**3)**



**i)** In this region  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COO}^-$  are both present.  $\text{CH}_3\text{COOH} / \text{CH}_3\text{COO}^-$  is a conjugate acid/base pair. When base is added to the buffer system it will react with  $\text{CH}_3\text{COOH}$ , thus maintain the pH by removing  $\text{OH}^-$ .

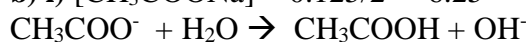


**ii)** X put on the graph at 10.00 mL

The most efficient buffering occurs when the pH of the solution is equal to  $\text{p}K_a$  ie  $[\text{HA}] = [\text{A}^-]$ .

Salt formed at equivalence point is  $\text{CH}_3\text{COONa}$ .

**b) i)**  $[\text{CH}_3\text{COONa}] = 0.125/2 = 6.25 \times 10^{-2} \text{ mol L}^{-1}$ .



$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

$$K_b = 10^{-9.24} = 5.75 \times 10^{-10}$$

$$5.75 \times 10^{-10} = \frac{[\text{OH}^-]^2}{6.25 \times 10^{-2}}$$

$$[\text{OH}^-] = \sqrt{3.596 \times 10^{-11}} = 5.997 \times 10^{-6}$$

$$[\text{H}_3\text{O}^+] = 1.667 \times 10^{-9}$$

$$\text{pH} = 8.78$$

**OR**

$$[\text{H}_3\text{O}^+] = \sqrt{\frac{K_a \times K_w}{c(\text{CH}_3\text{COO}^-)}}$$

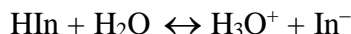
$$\frac{1.74 \times 10^{-5} \times 10^{-14}}{6.25 \times 10^{-2}} = 1.67 \times 10^{-9}$$

$$\text{pH} = 8.78$$

ii) Phenolphthalein is a suitable indicator as its  $\text{p}K_a$  is within 1 pH of equivalence point. Hence it will change colour at the equivalence point of the reaction in the steepest part of the graph.

Methyl orange will change colour in the buffer region as it's between pH 2.7 and 4.7 which is in the buffer region making this indicator unsuitable.

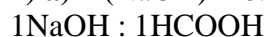
iii) Phenolphthalein is a weak acid and dissociates in water



When a base is added to the solution the equilibrium shifts in the forward direction. Therefore  $\text{In}^-$  is purple.

When acid is added the equilibrium shifts in the reverse direction, therefore  $\text{HIn}$  is colourless. Indicators are effective in the range  $\text{pH} = \pm 1 \text{ p}K_a$ , ie between 8.60 and 10.6.

$$4) \text{ a) } n(\text{NaOH}) = 0.180 \text{ mol L}^{-1} \times 0.04 \text{ L} = 0.0072 \text{ mol}$$



$$c(\text{HCOOH}) = 0.0072 \text{ mol} / 0.025 \text{ L} = 0.288 \text{ mol L}^{-1}$$



$$K_a = [\text{HCOO}^-][\text{H}_3\text{O}^+] / [\text{HCOOH}]$$

$$[\text{H}_3\text{O}^+] = \sqrt{(0.288 \text{ mol L}^{-1} \times 1.82 \times 10^{-4})} = 7.24 \times 10^{-3} \text{ mol L}^{-1}$$

$$\text{pH} = 2.14$$

b) Half way to the equivalence point (20 mL), the NaOH has reacted with half the  $\text{HCOOH}$ , so  $[\text{HCOOH}] = [\text{HCOO}^-]$ .

$$K_a = [\text{HCOO}^-][\text{H}_3\text{O}^+] / [\text{HCOOH}]$$

Since  $[\text{HCOOH}] = [\text{HCOO}^-]$ , substitution into  $K_a$  gives:

$$K_a = [\text{H}_3\text{O}^+]$$

Taking  $-\log$  of each side:

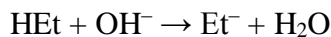
$$\text{p}K_a = \text{pH}$$

So the pH half way to the equivalence point =  $\text{p}K_a$  of  $\text{HCOOH} = 3.74$

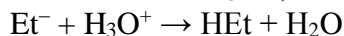
c) According to the titration curve, the pH at the equivalence point is approximately 8.4. Indicators change colour at their  $\text{p}K_a \pm 1$ . So bromocresol green changes colour over a pH range of 3.7-5.7 and alizarin yellow will change colour over a pH range of 10.0 – 12.0. This means bromocresol green would therefore change colour before the equivalence point and alizarin yellow would change colour after the equivalence point. Both of these indicators would therefore be unsuitable for this titration. Cresol red will change colour over a pH range of 7.3 – 9.3. This includes the pH at the equivalence point. Cresol red would therefore be a suitable indicator to detect the endpoint since it changes colour at the equivalence point.

**5) A**

At point A, there is an equi-molar mixture of HEt and Et<sup>-</sup>. On addition of OH<sup>-</sup> ions, the acid part of the buffer neutralises the OH<sup>-</sup> ions, by donating a proton. The acid reacts with the base:



On addition of H<sub>3</sub>O<sup>+</sup>, the ethanoate will accept a proton from the hydronium ion:

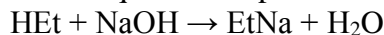


Candidate may discuss equilibrium shift.

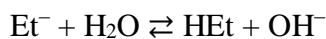
$$\text{p}K_a = \text{pH} = 4.76 \text{ (accept } 4.5 - 4.9)$$

**B**

At the equivalence point all the HEt has been neutralised by NaOH.



The Et<sup>-</sup> reacts further to a small extent with water.



Thus the pH of the equivalence point is above 7 due to presence of OH<sup>-</sup>.

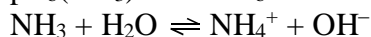
**6)** Since B is half way to the equivalence point,

$$[\text{NH}_4^+] = [\text{NH}_3]$$

$$K_a = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]} \text{ so } K_a = [\text{H}^+] \text{ p}K_a = \text{pH}$$

Note: [NH<sub>4</sub><sup>+</sup>] = [NH<sub>3</sub>] must include [ ] or the word **concentration**.

$$\text{p}K_b(\text{NH}_3) = 4.76 \quad K_b = 1.74 \times 10^{-5}$$



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{[\text{OH}^-]^2}{0.160}$$

$$[\text{OH}^-] = \sqrt{K_b \times [\text{NH}_3]} = 1.67 \times 10^{-3} \text{ mol L}^{-1}$$

$$\text{pOH} = 2.8 \text{ (accept } 2.77) \quad \text{pH} = \mathbf{11.2} \text{ (accept } 11.22)$$

OR

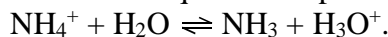
$$K_a = 5.75 \times 10^{-10}$$

$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = \frac{[\text{NH}_3] \times [\text{H}_3\text{O}^+]^2}{1 \times 10^{-14}}$$

$$[\text{H}_3\text{O}^+]^2 = \frac{5.75 \times 10^{-10} \times 10^{-14}}{0.160} = 3.59 \times 10^{-23}$$

$$[\text{H}_3\text{O}^+] = 5.99 \times 10^{-12} \text{ mol L}^{-1} \quad \text{pH} = 11.2 \text{ (accept } 11.22)$$

Solution at equivalence point is NH<sub>4</sub>Cl. This solution is weakly acidic since



so pH < 7.

**7)** C<sub>6</sub>H<sub>5</sub>COOH, C<sub>6</sub>H<sub>5</sub>COO<sup>-</sup>, OH<sup>-</sup>, Na<sup>+</sup> (Only one species in each box)

A buffer is a solution containing a weak acid and its conjugate base (or a weak base and its conjugate acid). It is able to resist changes in pH.

When 9.80 mL of base has been added, some of the benzoic acid has been converted to the benzoate ion (the conjugate base). There is still unreacted benzoic acid in the reaction vessel, so both acid and conjugate base are present together in reasonable / sufficient amounts. Hence the solution has buffering properties. When 25 mL of base has been added, the acid molecules have been converted to the conjugate base. The amount of benzoic acid is too low to have buffering properties.

Thymol blue or thymol blue and phenolphthalein would be best.

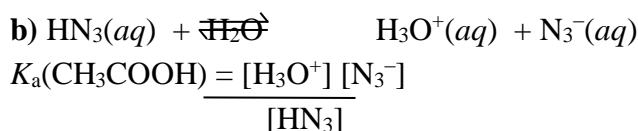
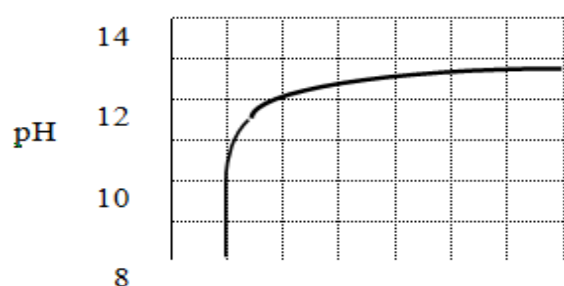
(May state thymol blue is best OR both thymol blue and phenolphthalein would be best depending on justification and pH value chosen)

A suitable indicator is one that has a  $pK_a$  and therefore its colour change at the equivalence point of the reaction indicated by the steep / vertical part of the curve. From the graph, the equivalence point is about 8.3. Both thymol blue and phenolphthalein are suitable because their  $pK_a$  values are within 1 of the equivalence point.

Methyl orange is unsuitable because it will change colour before the equivalence point is reached / volume indicated will incorrect / give wrong answer.

8) X drawn **on curve** at pH 9 (accept 8.5–9.5).

End of graph is drawn towards an asymptote line at pH 13.



pH = 2.6 so  $[\text{H}_3\text{O}^+(aq)] = 2.51 \times 10^{-3} \text{ mol L}^{-1} = [\text{N}_3^-(aq)]$

$pK_a(\text{HN}_3) = 4.72$ ,  $K_a(\text{HN}_3) = 1.91 \times 10^{-5}$

$$K_a(\text{HN}_3) = 1.91 \times 10^{-5} = \frac{(2.51 \times 10^{-3})^2}{x}$$

$x = 0.331$  ie  $[\text{HN}_3(aq)] = 0.331 \text{ mol L}^{-1}$  (Allow 0.330 and 0.33)

9) a) i)  $n(\text{NaOH}) = \frac{40}{1000} \times 0.160 = 6.40 \times 10^{-3} \text{ mol}$

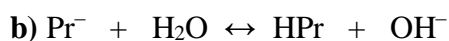
$n(\text{HPr}) = 6.40 \times 10^{-3} \text{ mol}$

$c(\text{HPr}) = \frac{1000}{50} \times 6.40 \times 10^{-3} = 0.128 \text{ mol L}^{-1}$

ii)  $K_a = 1.35 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{Pr}^-]}{[\text{HPr}]}$

$[\text{H}_3\text{O}^+]^2 = 1.35 \times 10^{-5} \times 0.128 = 1.728 \times 10^{-6}$

$[\text{H}_3\text{O}^+] = 1.32 \times 10^{-3} \text{ mol L}^{-1}$  pH = 2.88



$[\text{Pr}^-] = 6.40 \times 10^{-3} \times \frac{1000}{90} = 0.0711 \text{ mol L}^{-1}$

$$K_a = 1.35 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{Pr}^-]}{[\text{HPr}]} = \frac{[\text{H}_3\text{O}^+] \times 0.0711 \times [\text{H}_3\text{O}^+]}{10^{-14}}$$

$$[\text{H}_3\text{O}^+]^2 = \frac{1.35 \times 10^{-5} \times 10^{-14}}{0.0711} = 1.90 \times 10^{-18}$$

$$[\text{H}_3\text{O}^+] = 1.38 \times 10^{-9} \text{ mol L}^{-1} \quad \text{pH} = 8.86$$

**OR**

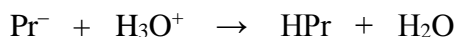
$$K_b = [\text{OH}^-]^2 / [\text{Pr}^-] = K_w / K_a \quad [\text{Pr}^-] = 0.128 \times 50/90 = 0.711 \text{ mol L}^{-1}$$

$$[\text{OH}^-] = \sqrt{1 \times 10^{-14} \times 0.711 / 1.35 \times 10^{-5}} = 7.25 \times 10^{-6} \text{ mol L}^{-1}$$

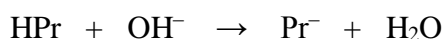
$$\text{pOH} = 5.14 \quad \text{pH} = 8.86$$

**c) i)** A buffer is a solution that undergoes minimal change of pH when small amounts of strong acid or base are added. In order to do this the buffer must contain species capable of reacting with the added acid or base.

**ii)** In this system added acid would need to react with  $\text{Pr}^-$  ions



and added base would need to react with HPr



Since 40 mL of sodium hydroxide is needed to exactly react with the propanoic acid, when 35 mL have been added, most of the propanoic acid has reacted and formed  $\text{Pr}^-$ .

So although the solution will buffer added acid it will not be very effective if base is added. So the solution would not be a good buffer.

**d)** Thymol blue or phenolphthalein are the best indicators because the pH range for the colour change will be approx  $8.9 \pm 1$ .

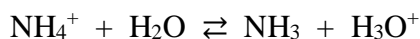
This lies within the range of the equivalence point ie the vertical portion of the graph / the portion where there is a large change in pH.

**10) a)**  $\text{p}K_a(\text{NH}_4^+) = 9.2 - 9.3$

$$K_a(\text{NH}_4^+) = 10^{-9.2} = 6.3 \times 10^{-10}$$

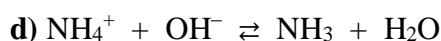
**OR**  $5.01 \times 10^{-10}$

**b)** At equivalence point all the  $\text{NH}_3$  has been converted to  $\text{NH}_4^+$  which reacts with water to produce  $\text{H}_3\text{O}^+$  ions and hence acidic solution.

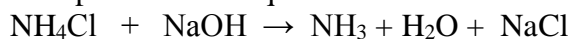


**c)** pH of 9.6 occurs after 3 mL – 4 mL  $0.200 \text{ mol L}^{-1}$  HCl has been added.

To 40.00 mL of  $0.0500 \text{ mol L}^{-1}$   $\text{NH}_3$  add 3.00 mL – 4.00 mL  $0.2 \text{ mol L}^{-1}$  HCl solution.



Accept molecular equations.



**e) i)** At equivalence point

$$n(\text{NH}_3) = 0.0400 \times 0.0500$$

$$V = 50 \text{ mL} = 0.050 \text{ L}$$

$$c(\text{NH}_3) = 0.04 \text{ mol L}^{-1}$$

At equivalence point all  $\text{NH}_4^+$  converted to  $\text{NH}_3$

$$c(\text{NH}_4^+) \text{ at start} = 0.0500 \text{ mol L}^{-1}$$

$$c(\text{NH}_3) \text{ at finish} = 0.0500 \times 40/50$$

$$= 0.0400 \text{ mol L}^{-1}$$

**ii)**  $[\text{H}_3\text{O}^+]^2 = \frac{1 \times 10^{-14} \times 6.3 \times 10^{-10}}{0.04}$

$$[\text{H}_3\text{O}^+] = 1.26 \times 10^{-11}$$

$$\text{pH} = 10.9$$